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The Solvent Effect on the Visible Absorption Spectra of the Radical Anion and the Dianion of Anthraquinone[1]

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In a previous work,[2] the half-wave potentials of anthraquinone were found to shift to more positive potentials with an increase in the water content in the DMF-alkaline water system. This behavior was interpreted in terms of the hydrogen-bonding of the radical anion or the dianion with water. On the other hand, the change in the hyperfine coupling constants in the ESR spectra of the radical anions[3-6] has been interpreted also in terms of the hydrogen-bonding of the radial anions with hydroxylic solvents, and a quantitative treatment has been given by Fraenkel *et al.*[5] The present work will deal with this hydrogen-bonding from the viewpoint of the solvent effect on the visible absorption spectra of the radical anion and the dianion of anthraquinone and with the correlation between the solvent shift of the visible absorption spectra of the anions and the change in the half-wave potentials.

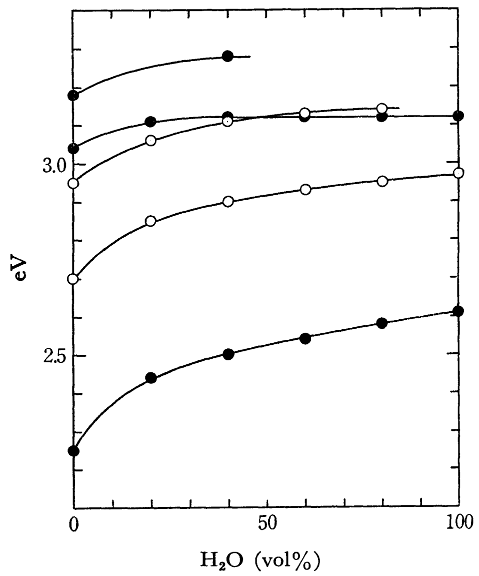

Fig. 1. Variations of λ_{max} of anthraquinone anions with the water content in the DMF - alkaline water system.
● $AQ^{\cdot-}$, ○ AQ^{2-}.

Experimental

The radical anion and the dianion of anthraquinone in the DMF-alkaline water system were generated by controlled-potential electrolysis.[7] The measurements of the visible absorption spectra of the anions were the same as have been described in a previous paper.[7]

Results and Discussion

In DMF containing 0.1 N tetraethylammonium perchlorate (TEAP) as the supporting electrolyte, the absorption maxima of $AQ^{\cdot-}$ were 390, 410, and 553 mμ[7] and those of AQ^{2-} were 420 and 460 mμ. Every visible absorption maximum showed a strong blue shift with an increase in the water content, as is shown in Fig. 1. The results for the radical anion are consistent with the λ_{max} values of 410 and 555 mμ in DMF[8] and with the λ_{max} values of 400 and 480 mμ in an ethylene glycol - alkaline water system.[9] As the molar extinction coefficients for these visible absorption bands were of the order of 10^4,[7] these intense

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[1] Presented at the 15th symposium of polarography, Sendai, Oct. 7, 1969.

[2] S. Hayano and M. Fujihira, This Bulletin, **44**, 2051 (1971).

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[4] Y. Deguchi, This Bulletin, **35**, 260 (1962); K. Umemoto, Y. Deguchi, and H. Takaki, *ibid.*, **36**, 560 (1963).

[5] J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2832 (1962).

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[7] S. Hayano and M. Fujihira, This Bulletin, **44**, 1496 (1971).

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absorption bands are presumably due to the $\pi\rightarrow\pi^*$ allowed transition.[10,11]

The blue shifts are similar not only to the change in the hyperfine coupling constants in the ESR spectra,[12] but also to the change in the half-wave potentials.[2] The changes are sharp for small quantities of water, but they gradually level out. The changes in the transition energies of $AQ^{\overline{\cdot}}$ and AQ^{2-} were compared with the changes in the half-wave potentials[2] of the first and the second waves respectively. There exists a linear relation between them, as is shown in Fig. 2. Such a relation suggests that both solvent shifts have the same cause, *i.e.*, hydrogen-bonding.

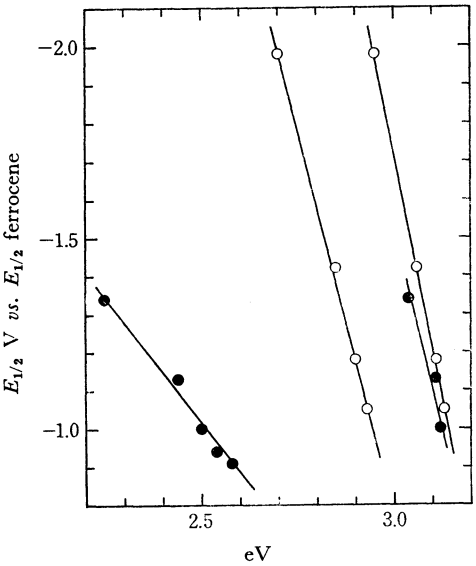


Fig. 2. Correlation between the solvent shifts of λ_{max} and those of $E_{1/2}$.
●, λ_{max} of $AQ^{\overline{\cdot}}$ *versus* $E_{1/2}$ of the first wave.
○, λ_{max} of AQ^{2-} *versus* $E_{1/2}$ of the second wave.

The electronic structures of hydrocarbon mono- and dinegative ions have been studied considerably,[13] but no theoretical investigations of those of mono- and dinegative ions of quinones have ever been made except for that of the *p*-benzosemiquinone ion.[11] Thus, we performed the HMO calculations in order to interpret the behavior qualitatively. The oxygen atoms of the anions are expected to be more electronegative in protic solvents, such as water and alcohol, than in aprotic solvents.[5] The Coulomb integral for the oxygen atom was varied in the calculations, since the change in the electronegativity of the oxygen atoms corresponds to the variation in the Coulomb integral for the oxygen atoms.[5] The variations in the energy levels with the change in the values of the parameter, δ, in the $\alpha_0=\alpha+\delta\beta$ relation for the Coulomb integral of the oxygen atom are shown in Fig. 3. The highest occupied energy level of the mono- and dinegative ions of $b_{3g}{}^*$ is found to be lowered remarkably with an increase in the values of δ. Thus, it is clear from such a simple calculation that the blue shift of λ_{max} and the positive shift of $E_{1/2}$ with the increase in the water content can be interpreted in terms of the hydrogen-bonding.

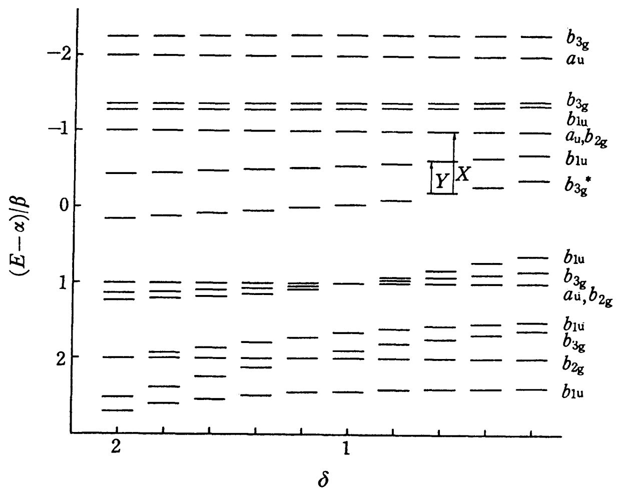
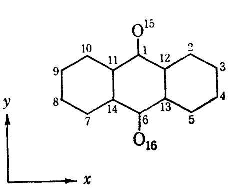


Fig. 3. Variations of the energy levels of anthraquinone with the change in the Coulomb integral for the oxygen atoms. The Coulomb and resonance integrals are assumed as follows:[14,15]



$\alpha_{12}=\alpha_2=\alpha_3=\alpha \quad \alpha_1=\alpha+0.2\beta$
$\alpha_0=\alpha+\delta\beta$
$\beta_{1-15}=\beta_{12-13}=\beta_{12-2}=\beta_{2-3}=\beta_{3-4}=\beta$
$\beta_{1-12}=0.8\beta$

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[11] Y. Harada, *ibid.*, **8**, 273 (1964).

[12] J. Q. Chambers and R. N. Adams, *ibid.*, **9**, 413 (1965).

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[14] A. Kuboyama, This Bulletin, **31**, 752 (1958).

[15] Fraenkel *et al.*[5] adjusted α_0 and β_{1-15} by varying the parameters δ and γ in the relations $\alpha_0=\alpha+\delta\beta$ and $\beta_{1-15}=\gamma\beta$ in an attempt to fit the proton splittings observed from the radical anions in ethanol - water system. The best values were found to be $\delta=0.9$ and $\gamma=1.4$. The HMO calculations were then performed in an attempt to fit the data for proton splittings in dimethylsulfoxide (DMSO) solution by adjusting the value of δ, while γ used for the ethanol - water system was left unchanged. The best value was found to be $\delta=0.4$ in DMSO. In the present work, other parameters except α_0 were quoted from Ref. 9, because the tendency was not affected very much by the choice of parameters.